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SULFUR DYE BATHS CONTAINING ALKALI METAL BOROHYDRIDES AND PROCESS OF DYEING CELLULOSE TEXTILES THEREWITH

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The present invention relates to an improved method of reducing sulfur dyes which reduction may or may not be in conjunction with dyeing of textile materials with the reduced sulfur dye. To the extent such reduction is in conjunction with dyeing, the present invention also relates to an improved method of dyeing cellulose textile materials with sulfur dyes.

Sulfur dyes are made, for the most part, by reacting sodium sulfide or elemental sulfur with nitro- or amino-substituted aromatic hydrocarbons, like benzene and naphthalene. The exact chemical structure of many sulfur dyes is not presently known. In their initial state they are insoluble in water, and can be converted to water-soluble form. Conversion of the insoluble form to the water soluble form may still not render the dye substantive toward cellulosic fibers, and the water-soluble but insubstantive form many require reduction to the substantive form. The stated conversions have been accomplished through reduction with sodium suulfide (Na_2S) or sodium sulfhydrate (NaHS) in alkaline medium. There are other well known water-soluble, but insubstantive, forms of sulfur dyes available, such as the bisulfite adducts.

The conversions may take place entirely separate and apart from any dyeing operation, and solely to provide the dye in marketable form, such as an aqueous solution of the sulfur dye in water-soluble, cellulose-insubstantive form or in water-soluble, cellulose substantive form. On the other hand, at least a portion of the conversion may take place as part of, or in conjunction with, a dyeing operation. For example, the sulfur dye in water-insoluble form or in water-soluble, cellulose-insubstantive form, may be applied to the cellulosic textile material following which it is reduced to cellulose-substantive form. Eventually the dye on the textile material is oxidized back to its insoluble form.

The foregoing has certain limitations which, if reduced or overcome, could greatly improve the use of sulfur dyes. For instance, conventional reduction of sulfur dyes to substantive form results in a differential in dye exhaustion on cloth dyed therewith, such as between the neps and the rest of the cloth being dyed. In addition, in conventional dyeing with sulfur dyes there is a tendency, during the subsequent oxidation step using a chromium-containing oxidizing agent, to form insoluble complexes therewith. These complexes tend to make the cloth harsh and difficult to rewet thus creating problems in finishing the cloth or in reworking cloth which has been dyed unsatisfactorily.

It is the principal object of the present invention to provide an improved method for reducing sulfur dyes.

It is another object of the present invention to provide an improved method for dyeing cellulosic textile materials with sulfur dyes.

Other objects will become apparent from a consideration of the following specification and claims.

The present invention comprises, in the reduction of a sulfur dye involving contacting said dye with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium, the improvement comprising the step of including with said sulfur-containing reducing agent in contacting said dye, an alkali metal borohydride. By the

present invention, the sulfur dye may be reduced from water-insoluble, cellulose-insubstantive form to water-soluble, cellulose-substantive form, or the dye may simply be reduced from water-soluble, cellulose-insubstantive form to water-soluble, cellulose-substantive form. The reduction, by the present invention, may take place in conjunction with a dyeing operation, as by applying, to the cellulosic textile material, the sulfur dye in water-insoluble form or in water-soluble, cellulose-insubstantive form, and then reducing the dye, according to the present invention, to cellulose-substantive form. The term "dyeing" as used herein includes localized dyeing, that is printing, as well as overall dyeing.

All of the operations, conditions and features, including any pre- or post treatments of cellulosic textile material being dyed, except for the presence of the borohydride during reduction of the sulfur dye and the consequent advantages flowing from its use—including a possible reduction in the amount of sodium sulfide or sodium sulfhydrate required—form no part of the present invention, since they may be conventional.

Thus the reduction will take place in aqueous medium in which the concentration of sodium sulfide or sodium sulfhydrate may depend upon the extent of reduction and upon the concentration of dye or dyes, which in turn may depend upon the intensity of dyeing desired. The temperature of the reduction medium may vary from ambient or room temperature to elevated temperatures, even as high as 230° F., and the exact temperature may be dictated by the particular dyeing technique used, when the reduction takes place in conjunction with a dyeing operation. For example, the reduction medium may be applied to the dye-containing textile material at room temperature following which the material may be heated, as by steaming. Likewise, as is known, the medium in which the reduction takes place will be alkaline, usually at a pH of at least 9.5. This is normally provided by the addition of a water soluble base, usually an alkali metal salt or hydroxide, like sodium carbonate or sodium hydroxide.

With respect to the borohydride, it may be any of the alkali metal borohydrides, especially those of sodium or potassium. Sodium borohydride is presently preferred. The amount of borohydride employed may vary somewhat, depending upon the amount of sulfur dye and upon the conditions, including time and temperature, of exposure of the reduced sulfur dye to oxidation, such as from air, in the particular system used as will be understood by those skilled in the art. Amounts of borohydride between about 0.01% and about 1%, preferably between about 0.1% and about 0.6%, by weight, based on the weight of the sulfur dye may be used.

As stated, the reduction may take place separate and apart from any dyeing operation in which case the borohydride along with the sulfur-containing reducing agent, may simply be mixed with the sulfur dye to be reduced. The mixing will take place in water, with sufficient base being included to provide the desired alkaline pH. The reduced sulfur dye, in water-soluble, substantive form, may subsequently be applied to the cellulosic textile material.

A sulfur dye solution containing the dye in substantive form, prepared according to conventional methods, and containing the stated sulfur-containing reducing agent, may be somewhat unstable, particularly during handling and use, with a tendency for the dye to revert to insubstantive form. Thus, in accordance with a further embodiment, an alkali metal borohydride may be added to such a sulfur dye solution, before marketing or at least before application to the cellulosic textile material, to maintain the dye in substantive form.

If the reduction takes place in conjunction with a dyeing operation, the cellulosic textile material containing sulfur dye in cellulosic-insubstantive form is contacted with the reducing medium to reduce the dye to cellulose-substantive form. Thus, the sulfur dye may be applied to the cellulosic textile material in water-insoluble form or in water-soluble but insubstantive form and then reduced to substantive form according to the present invention. As is well known, the cellulosic textile material may or may not be dried or partially dried between application of the sulfur dye and contact with the reducing medium. If the dye in substantive form is applied to the textile material which is then subjected to a dyeing operation, some or all of the dye can revert to insubstantive form before contact with the reducing medium. Such textile material, containing sulfur dye in insubstantive form, may be treated in accordance with the present invention to reduce the insubstantive form of the sulfur dye to substantive form. Once the dye is on the cellulosic textile material in cellulose-substantive form, further treatment, such as rinsing, oxidizing, rinsing, soaping, rinsing, drying, and so on, proceeds in the conventional manner.

The sulfur dye bath may contain the usual additives, such as Glauber's salt, thickeners, surfactants, and the like.

Reference has been made herein to the dyeing of cellulosic textile material. This will be understood to include regenerated cellulose as well as cotton, in the form of fibers, filaments, yarns or cloth, in which the cellulosic material may be the sole textile material present or is admixed with other, noncellulosic, materials.

As stated previously, the chemical formula of many sulfur dyes is presently unknown, although they are prepared by fusion of sulfur or sodium sulfides with an aromatic hydrocarbon, usually benzene or naphthalene, containing amino- and/or nitro-substituents. One water-soluble, cellulosic-insubstantive form is believed to be a bisulfite adduct of the water-insoluble form. The sulfur dyes, either in water-insoluble form or water-soluble, but cellulose-insubstantive form, are set forth in the Colour Index of The American Association of Textile Chemists and Colorists, Lowell Technological Institute, Lowell, Mass. Examples of sulfur dyes in water-insoluble form are ("C.I." means Colour Index):

C.I. 53040—C.I. Sulfur Yellow 1
C.I. 53160—C.I. Sulfur Yellow 4
C.I. 53235—C.I. Sulfur Blue 5
C.I. 53440—C.I. Sulfur Blue 7
C.I. 53571—C.I. Sulfur Green 2
C.I. 53055—C.I. Sulfur Brown 10
C.I. 53246—C.I. Sulfur Brown 14
C.I. 53830—C.I. Sulfur Red 5
C.I. 53185—C.I. Sulfur Black 1

Examples of sulfur dyes in water-soluble, but cellulose-insubstantive, form are:

C.I. 53120—C.I. Solubilized Sulfur Yellow 2
C.I. 53225—C.I. Solubilized Sulfur Yellow 8
C.I. 53185—C.I. Solubilized Sulfur Black 1
C.I. 53000—C.I. Solubilized Sulfur Brown 1
C.I. 53440—C.I. Solubilized Sulfur Blue 7
C.I. 53721—C.I. Solubilized Sulfur Brown 12
C.I. 53270—C.I. Solubilized Sulfur Brown 15
C.I. 53571—C.I. Solubilized Sulfur Green 2
C.I. 53570—C.I. Solubilized Sulfur Green 3
C.I. 53327—C.I. Solubilized Sulfur Brown 51
C.I. 53005—C.I. Solubilized Sulfur Green 9
C.I. 53470—C.I. Solubilized Sulfur Blue 10
C.I. 53480—C.I. Solubilized Sulfur Blue 2
C.I. 53055—C.I. Solubilized Sulfur Brown 10

The following examples are given for the purpose of illustration only and are not intended to limit the scope of the invention in any way:

Example I

In this example sulfur dyes, in water-soluble, cellulose-insubstantive form, are reduced to cellulose-substantive form using sodium sulfide and a borohydride. The reduction takes place in conjunction with a dyeing operation during which are dyed a total of 26,526 yards of cotton cloth as follows:

Yards	Greige—Construction		
15,028	47½″	100/58	3.07
5,000	47″	136/60	3.10
6,498	47″	109/58	2.84

The cloth is preliminarily treated in a conventional manner, including singeing, desizing, kier boiling, mercerizing, bleaching (hypochlorite) and drying.

The sulfur dye is then applied by padding, in a conventional manner. The dye bath is an aqueous solution, at 120° F., made up of the following:

281.6 lbs. C.I. Solubilized Sulfur Brown 1
128.7 lbs. C.I. Solubilized Sulfur Brown 12
17.6 lbs. C.I. Solubilized Sulfur Black 1
Water to make 750 gallons

Following application of the dye, the cloth is dried in a hot flue dryer. An aqueous solution of the following reducing medium is then applied by padding, at 90° F., in a conventional manner:

150 lbs. sodium sulfide
100 lbs. sodium carbonate
1.875 lbs. sodium borohydride
6.5 lbs. sodium hydroxide
Water to make 750 gallons

The cloth is then steamed, at about 225° F., for 25 seconds, rinsed, oxidized with sodium bichromate and acetic acid, rinsed again, soaped with detergent and sodium carbonate, rinsed again and dried, all according to conventional procedure.

The dyed cloth is extremely level in appearance, shows less "neppiness" and has improved rewettability in subsequent resin-finishing, as compared to the same material treated in the same manner but omitting the borohydride. The dyed cloth is also markedly free from bronziness. The shade uniformity of the run is excellent and shows less variation than that normally anticipated.

Example II

In this example sulfur dyes, in water-soluble, cellulose-insubstantive form, are reduced to cellulose-substantive form with sodium sulfhydrate and borohydride. The reduction is in conjunction with a dyeing operation as in Example I.

A solution of 3 oz./gal. C.I. Solubilized Sulfur Brown 51 and 1 oz./gal. C.I. Solubilized Sulfur Green 9, in water, at 140° F., is padded onto 41″ 78/78 4.05 cotton cloth to 70% pickup. The cloth is then dried in a hot flue dryer.

An aqueous solution containing 2.4%, by weight, sodium sulfhydrate; 0.8% sodium carbonate; 0.05% sodium borohydride, and 0.16% sodium hydroxide, at 90° F., is then padded onto the cloth. The cloth is then steamed, at about 225° F., for 30 seconds, rinsed, oxidized with sodium bichromate and acetic acid, rinsed, soaped, rinsed and dried, all according to conventional procedure. The results are comparable to those obtained in Example I.

Example III

In this example water-insoluble sulfur dyes are reduced to water-soluble, cellulose-substantive form using sodium sulfide and borohydride.

A mixture of 6 oz./gal. of C.I. Sulfur Brown 37 and 2 oz./gal. of C.I. Sulfur Green 16, in water, at 140° F., is padded onto 41" 78/78 4.05 cotton cloth to 70% pick-up. The cloth is then dried in a hot flue dryer.

An aqueous solution containing 2.4%, by weight, of sodium sulfide; 0.8% sodium carbonate; 0.05% sodium borohydride, and 0.16% sodium hydroxide, is then padded, at 100° F., onto the cloth. The cloth is steamed, at about 225° F., for 30 seconds, rinsed, oxidized with sodium bichromate and acetic acid, rinsed, soaped, rinsed and dried, all according to conventional procedure. The results are comparable to those obtained in Example I.

Example IV

In this example water-insoluble sulfur dyes are reduced to water-soluble, cellulose-substantive form using sodium sulfhydrate and borohydride.

The procedure of Example III is followed with 2.4% sodium sulfhydrate, instead of sodium sulfide, in the reducing bath, and using the following mixture of dyes:

16 oz./gal. of C.I. Sulfur Green 16
7.3 oz./gal. of C.I. Sulfur Yellow 4

The results are comparable to those obtained in Example I.

Modification is possible in the selection of particular conditions, amounts of materials and techniques without departing from the scope of the invention.

I claim:

1. In the reduction of a sulfur dye involving contacting said dye with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium, the improvement comprising the step of including with said sulfur-containing reducing agent in contacting said dye, an alkali metal borohydride.

2. The method of claim 1 wherein said alkali metal borohydride comprises sodium borohydride.

3. In the reduction of a sulfur dye from water-insoluble form to water-soluble, cellulose-substantive form involving contacting said dye with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium, the improvement comprising the step of including with said sulfur-containing reducing agent in contacting said dye, an alkali metal borohydride.

4. In the reduction of a sulfur dye from water-soluble, cellulose-insubstantive form to cellulose-substantive form involving contacting said dye with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium, the improvement comprising the step of including with said sulfur-containing reducing agent in contacting said sulfur dye, an alkali metal borohydride.

5. In the dyeing of cellulosic textile material with a sulfur dye involving contacting said dye with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium to reduce the dye to water-soluble, cellulose-substantive form, the improvement comprising the step of including with said sulfur-containing reducing agent in contacting said dye, an alkali metal borohydride.

6. The method of claim 5 wherein said alkali metal borohydride comprises sodium borohydride.

7. In the dyeing of cellulosic textile material with a sulfur dye involving applying to said material a sulfur dye in cellulose-insubstantive form and thereafter contacting said dye-containing material with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium to reduce said dye to cellulose-substantive form, the improvement comprising the step of including with said sulfur-containing reducing agent in contacting said dye-containing material, an alkali metal borohydride.

8. The method of claim 7 wherein said alkali metal borohydride comprises sodium borohydride.

9. In the dyeing of cellulosic textile material with a sulfur dye involving contacting said dye, in cellulose-insubstantive form, with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium to reduce said dye to cellulose-substantive form and thereafter applying said dye in cellulose-substantive form to cellulosic textile material, the improvement comprising the step of including with said sulfur-containing reducing agent in contacting said dye, an alkali metal borohydride.

10. The method of claim 1 wherein said borohydride is present in an amount between about 0.01 and about 1%, by weight, based on the weight of the sulfur dye.

11. The method of claim 1 wherein said borohydride is present in an amount between about 0.1 and about 0.6%, by weight, based on the weight of the sulfur dye.

12. In an alkaline aqueous solution of a sulfur dye in water-soluble, cellulose-substantive form containing also a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate, the improvement comprising an alkali metal borohydride in said solution with said dye and said sulfur-containing reducing agent.

13. The composition of claim 12 having a pH above 9.5.

14. In the preparation of an aqueous solution of a sulfur dye in water-soluble, cellulose-substantive form involving reducing a sulfur dye form cellulose-insubstantive form to cellulose-substantive form with a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate in alkaline medium, the improvement which comprises adding to said solution an alkali metal borohydride.

15. In the dyeing of cellulosic textile material with sulfur dye involving applying to said material an aqueous alkaline solution containing sulfur dye in cellulose-substantive form and a sulfur-containing reducing agent selected from the group consisting of sodium sulfide and sodium sulfhydrate, the improvement comprising the step of adding to said solution, before application to said material, an alkali metal borohydride.

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